



# Dynamic tuning of naked ruthenium clusters/nanoparticles in ionic liquids cages to boost CO<sub>2</sub> hydrogenation to formic acid

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## ARTICLE INFO

### Keywords:

Ruthenium clusters  
Carbon dioxide  
Selective hydrogenation  
Ionic liquids cages  
SILPs

## ABSTRACT

The reduction of atmospheric CO<sub>2</sub> is indeed a major challenge for modern life due to its increase as a result of the intensified contemporary industrial activities and its contribution to global warming. One of the most desirable approaches to accomplish this goal is to convert CO<sub>2</sub> into C1 feedstocks, such as formic acid (FA). In this regard, naked ruthenium clusters and nanoparticles (1.8 ± 0.3 nm) are prepared by magnetron sputtering into different supported ionic liquid phases (SILPs) that demonstrated remarkable efficiency in producing a total of 2.2 M of free FA with a TONs of 7305 in 1-Butyl-3-methylimidazolium acetate ionic liquid media at 87 °C. The higher efficiency is related to the hydrophobic/hydrophilic effect presents in the ionic liquid-cages of the SILPs akin to the micelle nano (micro)reactors, which act as catalytic membranes enabling the tuning of FA production. DFT calculations support the mechanistic approach followed the hydrogenation of HCO<sub>3</sub><sup>-</sup> to FA.

## 1. Introduction

Emissions of carbon dioxide have received worldwide attention because of the environmental and economic threats posed by climate change [1,2]. The reduction of CO<sub>2</sub> as well as its conversion to value added chemicals and fuels is the main challenge facing research community. Although pure CO<sub>2</sub> can be obtained from the atmosphere by the CO<sub>2</sub> capture technologies such as absorption, adsorption, cryogenics, and membrane separation [3,4]. But its transportation and storage process is at economic and energy cost [5]. One of the best ways is to utilize and convert it (catalytically) into the sustainable valuable commodities such as formic acid (FA), methanol, higher hydrocarbons, carbonates (cyclic), formaldehyde, dimethyl ether and carbon monoxide thermally and photochemically [5–11]. Among them, by coupling the hydrogen and CO<sub>2</sub> into FA addresses to realize a hydrogen-based economy. FA is attractive hydrogen carrier with the volumetric H<sub>2</sub>

density of 53 g of H<sub>2</sub>/litre [12].

Capturing and activating CO<sub>2</sub> with ionic liquids (ILs) is a highly promising approach among the various emerging technologies aimed for dealing with the increasing CO<sub>2</sub> emissions [13,14]. The unique properties of ILs offer advantages during the hydrogenation of CO<sub>2</sub>, as evidenced by the recent activity in this area [15–21]. ILs specially the imidazolium ones can generate the solvent “cage” around the catalysts (NPs, complexes and enzyme) akin to the micelle nano (micro)reactors, that can selectively control the diffusion of reactants, intermediates, and products, mainly through their hydrophobicity and contact ion pairs to the catalytically active sites [22–27]. This cage effect was revealed several times in reactions performed in both bare ILs and hybrids containing ILs [25,28]. However, there is still a lack of understanding regarding the correlation between the IL-catalyst structure and performance during CO<sub>2</sub> reduction. In the clear majority of the cases the CO<sub>2</sub> hydrogenation is performed by homogenous based catalysts (Ru, Rh and

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Ir) in the presence of the bases producing formates but not free formic acid. Amines functionalized ILs with ruthenium complexes have been studied that hydrogenate CO<sub>2</sub> exclusively to formate salts (not FA) [29–31]. Recently, homogeneous system based on Ru-complexes with sophisticated ligands have been reported to generate FA in BMIm.OAc IL system and represented activity from few thousands to several thousand TONs ( $1950\text{--}8 \times 10^5$ ) [16,32–34]. Only in a few cases the hydrogenation of CO<sub>2</sub> has been performed by heterogeneous catalysts under severe reaction conditions (40 MPa) but generally with low catalytic performance [35–37]. CO<sub>2</sub> hydrogenation to free FA by well-defined metal nanoparticles is rare.

Moreover, the contribution of buffer-like solutions versus the Ru clusters/NPs during CO<sub>2</sub> hydrogenation is usually overlooked and not fully explored. It is usually assumed that the interaction of CO<sub>2</sub> with these ILs is related to the formation of cation- or anion-CO<sub>2</sub> adducts. Here, we show that the use of basic IL that forms buffer-like solutions with DMSO/aqueous media enables the selective catalytic hydrogenation of CO<sub>2</sub> through the naked Ru clusters/NPs, resulting in high efficiency production of the free FA (Scheme 1). In this contribution, surface-cleaned Ru clusters and NPs were prepared by magnetron sputtering into the SILPs. The hydrophilic and hydrophobic nature of the SILPs selectivity not only controlled the growth of the clusters/NPs but also governed the catalytic activity. We showed that the Ru clusters/SILPs displayed higher catalytic activity and selectivity to free FA (not formate salt) as compared to Ru NPs supported on pristine SiO<sub>2</sub>.

## 2. Experimental

HPLC grade solvents were purchased from Sigma-Aldrich chemicals. The 1-butyl-3-methyl-imidazolium acetate (BMIm.OAc) IL was synthesized as reported elsewhere [38,39]. Hydrogen (> 99.999 %) and carbon dioxide (> 99.999 %) were obtained from Air-liquid Ltd, Brazil. All the NMRs spectra were measured using a Bruker AVANCE III 500 MHz.

### 2.1. Sputtering depositions of Ru clusters/NPs onto SILPs

In a typical procedure, 2.0 g of SILP was placed in an aluminum conical Al flask inside a deposition chamber. Then, the pressure of the chamber was lowered to  $1.6 \times 10^{-6}$  mbar. Afterward, the pressure was raised to  $5.4 \times 10^{-2}$  mbar with argon at a flow rate of 5 mL/min. The deposition process took place with a power of 100 W, with a current of 225 mA per a time of 43 min. The flask was rotated at a frequency of 18 Hz to maintain continuous homogenization of the supports. After metal deposition, the argon was vented into chamber. The catalysts were

stored under an argon atmosphere for characterization and application.

Note: No free IL (BMIm.OAc) was added in SILP during sputtering deposition.

### 2.2. Evaluation of Catalytic performance

The catalytic experiments were evaluated in 25 mL Fischer-porter reactor made of stainless steel with a glass lining. stainless steel glass-lined Fischer-porter reactor. Typically, 20 mg of the catalyst was added in the solution of DMSO (2.84 g, 36.4 mmol), H<sub>2</sub>O (33 mg, 1.8 mmol) and IL. To eliminate atmospheric impurities, the reactor was flushed with CO<sub>2</sub>. Then the reactor was filled with 32 bar of gas mixture of CO<sub>2</sub> and H<sub>2</sub> (1:2) and the reaction was conducted at desire temperature and time in silicon oil bath. After the reaction, the reactor was cooled in ice-cold water and then cautiously vented. The produced FA was directly analyzed by <sup>1</sup>H NMRs using DMSO-d<sub>6</sub> solvent. TONs were calculated by mole of FA formed per mole of Ru surface atoms [40].

For the recyclability test, the catalyst was isolated through centrifugation, washed twice with 5 mL each of acetone and dichloromethane, and subsequently dried under vacuum at room temperature. Subsequently, the catalyst was added to a fresh IL solution to carry out CO<sub>2</sub> hydrogenation.

## 3. Results and discussion

### 3.1. Catalysts preparation and characterizations

Hydrophobic and hydrophilic SILPs supports were prepared by sol-gel process using 1-methyl-3-(3-trimethoxysilylpropyl)-imidazolium cations containing tetrafluoroborate (BF<sub>4</sub>) and bis(trifluoromethylsulfonyl)imide (NTf<sub>2</sub>) anions (Fig. 1) [41]. The introduction of BF<sub>4</sub> and NTf<sub>2</sub> anions generated the hydrophilic and hydrophobic

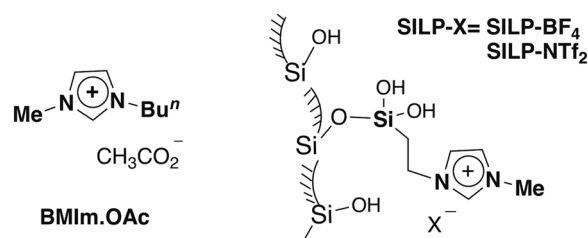
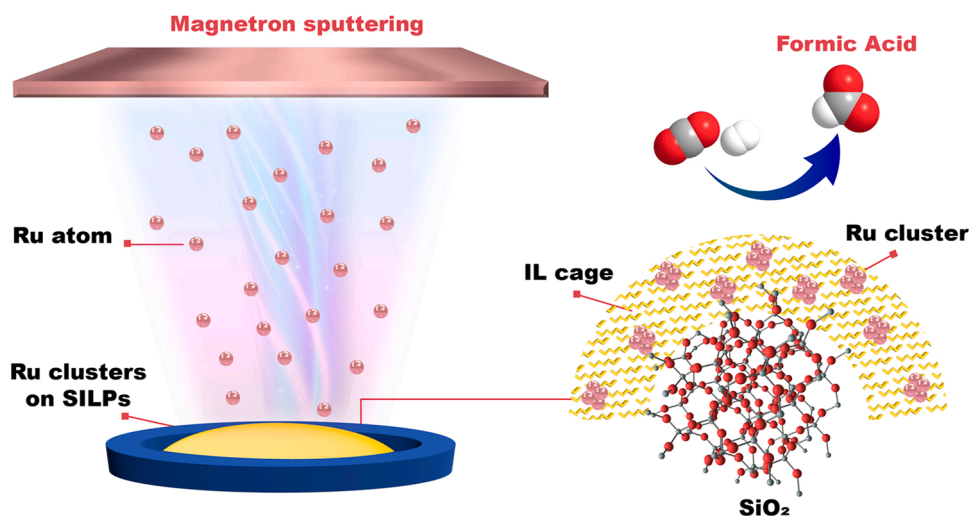


Fig. 1. Structure of SILPs and IL used in this study.



Scheme 1. Schematic representation of the preparation of naked Ru clusters/NPs into SILPs by magnetron sputtering and their CO<sub>2</sub> hydrogenation to “free” formic acid (FA).

properties in SILPs supports, respectively. Solid  $^{13}\text{C}$  and  $^{29}\text{Si}$  CP-MAS analyses were performed, which confirmed that the ILs were covalently bonded on  $\text{SiO}_2$  surface (Fig. S1-S2).

The prepared SILPs were decorated with Ru clusters/NPs by physical deposition employing a “vibrational” sputtering chamber (VSC) that allowed the constant mixing of the solid support during the deposition (Scheme 1) [42]. This method is very simple and allows the generation of “clean” surface MNPs since there are no other chemicals employed in the process [43]. The sputtering deposition of Ru onto SILPs was conducted using 223 mA discharge current to yield clusters and NPs. The presence of the Ru clusters and ultra-small NPs in the supports were confirmed by scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) of several particles (Figs. 2 and 3).

STEM-HAADF images represented that the visualization of ultra-small Ru NPs on the SILP- $\text{BF}_4$  support is not globally evident, small clusters with the size of  $1.02 \pm 0.6$  nm can be observed (Fig. 2a-b). In the regions where the support was not thick, clusters were detected. The EDS spectrum, even in regions where the Ru clusters were not directly observed, indicates the presence of the Ru element (Fig. 2c-d).

The formation of the Ru clusters and NPs in SILPs may follow the route akin to the thin-film growth on liquids that involves the nucleation, growth of the atomic clusters and aggregation into NPs/branched island [44–46]. ILs can kinetically control the nucleation of the NPs through the interaction between the incoming gaseous atoms and the chemical composition of the ILs [47,48]. The contact ion pair strength (cation-anion interaction) of the ILs can tune the size and shape of the NPs [49,50]. Hence, ILs are adequate media for the stabilization of single atom metal catalysts [51]. Molecular dynamic study showed that Pd clusters with their large induced dipole moments interact strongly with 1,3-dimethylimidazolium tetrafluoroborate (MMIm. $\text{BF}_4$ ) IL [52]. As a result,  $\text{BF}_4$  anion containing IL stabilized the clusters without their further growth to the NPs by providing the high density and a negative charge IL layer. Similar behavior of IL-anion ( $\text{BF}_4$ ) effect is observed in our case where the Ru clusters are formed on SILP having  $\text{BF}_4$  anion.

Extremely well distributed small Ru NPs of  $1.8 \pm 0.3$  nm were observed into the SILP- $\text{NTf}_2$  support (Fig. 3a). Whereas, relatively large sized  $2.1 \pm 0.6$  nm Ru NPs in aggregates were revealed into the pristine  $\text{SiO}_2$  under similar sputtering conditions (Fig. 3c). Global EDS proved the presence of Ru observed via Z-contrast in HAADF-STEM images (Fig. 3b-c). Of note that the presence of hydrophobic anion in SILP- $\text{NTf}_2$  caused the higher dispersion of Ru NPs. Whereas, agglomeration of Ru NPs was found into  $\text{SiO}_2$  where no IL was presented.

Fig. 4a compares the Rutherford backscattering spectrometry (RBS) spectra collected for all samples. The prominent peak observed in the

rising of the Ru plateau suggests a higher concentration of Ru on the samples' surface [53,54]. The surface enrichment with Ru atoms pointed by the RBS results depends on the SILPs properties. Ru/SILP- $\text{BF}_4$  presented sharper peaks as compared to the Ru/SILP- $\text{NTf}_2$  and Ru/ $\text{SiO}_2$ , indicating that  $\text{BF}_4$  containing IL favor the anchoring of Ru atoms near to the sample' surface. Moreover, the sample supported on pure  $\text{SiO}_2$  presented the most regular Ru plateau indicating a more uniform distribution of Ru atoms on  $\text{SiO}_2$  comparing to the samples prepared with IL-modified silica. The compositions of the samples were extracted from RBS (a bulk sensitive technique) data, leading to the Ru concentrations in samples' bulk presented in Table 1.

The compositions of samples' surfaces were extracted from the analysis of the X-ray photoelectron spectroscopy (XPS) survey scans (available in Fig. S6). The presence of small amounts of F was observed for all samples except in Ru/ $\text{SiO}_2$ , which represented the presence of IL in SILP- $\text{BF}_4$  and SILP- $\text{NTf}_2$ . Fig. 4 also indicates that IL-modified samples also have different concentrations of C on their surfaces. The contributions of ruthenium (Ru  $3p_{3/2}$  peak) and silicon (Si 2p region) were used to estimate the Ru concentration at the samples' surfaces, which were compared to RBS results as shown in Table 1. The ratio between Ru concentration at the samples' surface and at samples' bulk corroborates the qualitative analysis based on RBS data: the use of SILP- $\text{BF}_4$  lead to catalyst with Ru-rich surfaces as compared to the SILP- $\text{NTf}_2$  and, even more, to pristine  $\text{SiO}_2$  (Table 1). The chemical environment of Ru atoms at samples' surfaces was probed by high resolution XPS data collected at Ru 3p and Ru 3d regions. The main results and the parameters extracted from this analysis are available as ESI in Table S1. The Ru 3p doublet (Fig. 4b) was deconvoluted in two chemical components, whose BE and spin-orbit splitting are typical for  $\text{Ru}^0$  (metallic Ru) and  $\text{Ru}^{4+}$  ( $\text{RuO}_2$ ) [55,56]. The  $\text{Ru}^0$  component dominates all samples' spectra indicating that Ru atoms are mostly in their metallic state in all probed samples' surfaces. As indicated in Table S1, the contribution of  $\text{RuO}_2$  component is slightly higher for sample Ru/SILP- $\text{BF}_4$  (whose Ru atoms are mainly anchored at the surface and therefore more exposed) than for samples Ru/SILP- $\text{NTf}_2$  (in which the Ru distribution is in the depth).

The Ru 3d region has a strong overlap with C 1s region, which hinders the analysis of Ru 3d doublet, due to low Ru amount. Fig. 4c showed the photoemission data collected at Ru 3d + C 1s region for Ru/SILP- $\text{BF}_4$  and Ru/ $\text{SiO}_2$ , whose survey scans' analysis indicated the higher and lower amounts of Ru at the samples' surface, respectively. Although the C 1s signal dominates the 277–292 eV region, the structure observed at lower BE ( $\sim 281$  eV) in both Fig. 4c indicates the presence of Ru atoms at the surfaces of the all samples [20,57]. Moreover, the different intensity of this structure in each data set corroborates that the Ru amount varies between the samples. The chemical ambient of Ru and C atoms

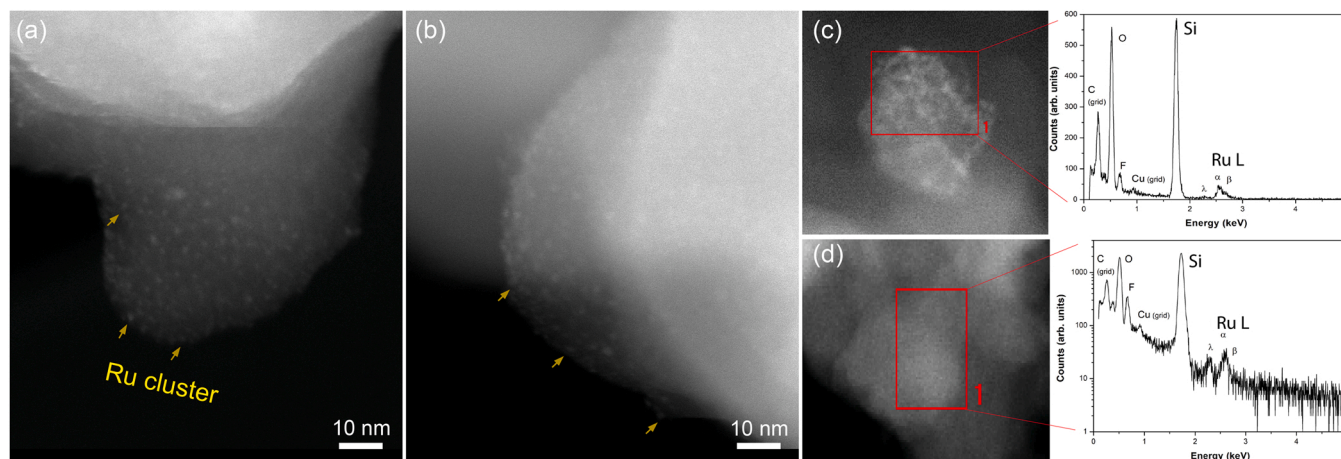


Fig. 2. (a,b) HAADF-STEM images of Ru clusters into SILP- $\text{BF}_4$ , (c) HAADF-STEM image and its EDS spectrum at linear scale position and (d) HAADF-STEM image and its EDS spectrum logarithmic scale.



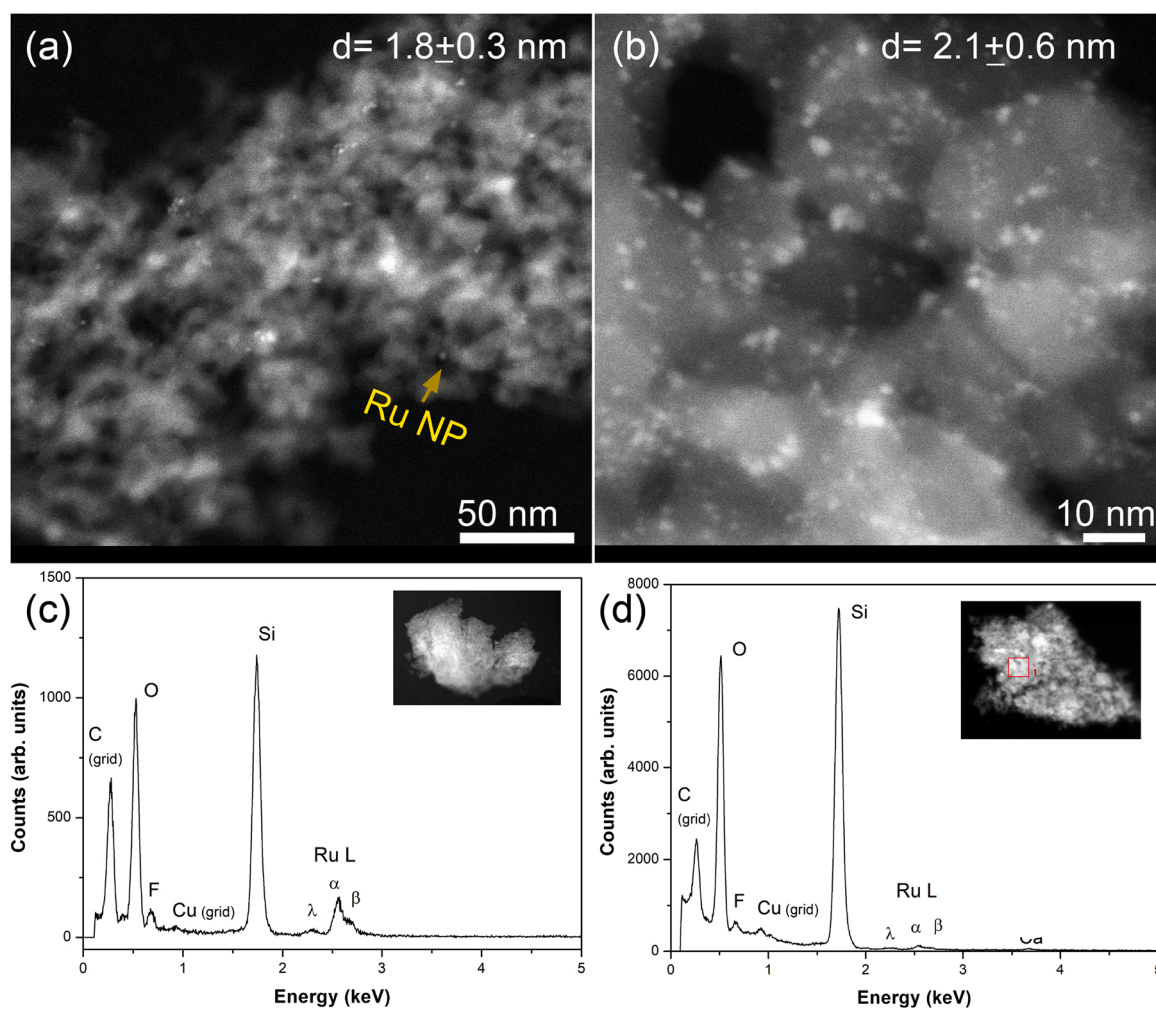


Fig. 3. HAADF-STEM images and EDS spectra of (a,b) Ru NPs into SILP-NTf<sub>2</sub> and (c,d) Ru NPs into pristine SiO<sub>2</sub>. (See more images in [supporting information](#)).

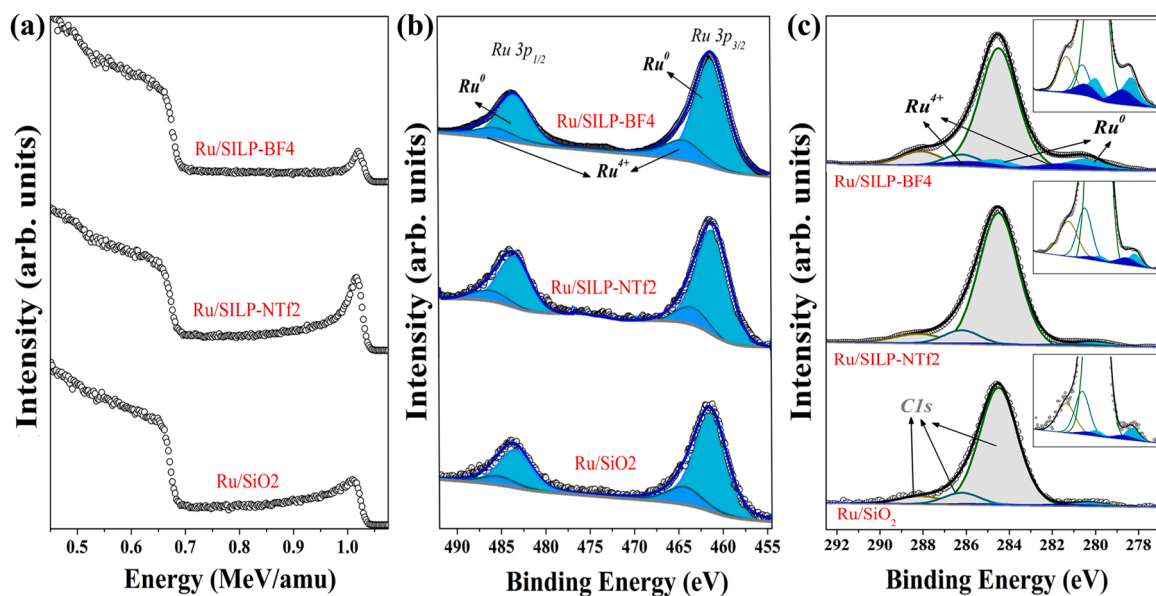


Fig. 4. (a) RBS data collected with 1.2 MeV He<sup>+</sup> beam incident on Ru-based samples. (b,c) XPS data (open circles), chemical components used in the analysis of Ru 3p and 3d regions (area-filled curves) and the resulting envelopes (blue lines).

**Table 1**

Ru concentrations obtained by RBS (bulk sensitive) and XPS (surface sensitive).

Catalyst	Ru concentration (wt%) <sup>a</sup>		Surface (XPS)/Bulk (RBS) Ratio
	Surface (by XPS)	Bulk (by RBS)	
Ru/SILP-BF <sub>4</sub>	28	3	9.3
Ru/SILP-NTf <sub>2</sub>	14	7	20
Ru/SiO <sub>2</sub>	12	8	1.5

[a] In the calculation of the Ru loadings in wt% the contributions of F and C were not taken in account.

were investigated through the data deconvolution in five components, whose BEs, FWHMs and relative areas are available in Table S1. For Ru 3d doublet, two chemical components (two doublets) were used and assigned to Ru<sup>0</sup> (280.2 and 284.4 eV) and Ru<sup>4+</sup> (281.5 and 285.8 eV). As well as in Ru 3p region, the metallic component dominates the Ru 3d region and the Ru oxidation is slightly higher for sample Ru/SILP-BF<sub>4</sub>. The inset graphs in Fig. 4c showed better these components for samples Ru/SILP-BF<sub>4</sub>, along with the relative areas of C 1s peak (sum of the three components), Ru<sup>0</sup> and Ru<sup>4+</sup> (Table S1) corroborates the changes in the surface amount of Ru indicated by the survey scan data analysis. Thus, the combined results from RBS and XPS indicated that samples supported on BF<sub>4</sub>-modified silica presented higher amounts of Ru at their surfaces as compared to the other samples (Table 1). The higher concentration of the surface Ru may be related to the hydrophilic nature and anion population on surface in IL [57]. It has been observed the relative concentration of alkyl chain and BF<sub>4</sub> anion on the IL surface is higher than the alkyl chain and NTf<sub>2</sub> anion [58]. As a result the penetration of Ru atom into the IL-bulk is low in the SILP-BF<sub>4</sub>.

### 3.2. Catalytic performance of CO<sub>2</sub> hydrogenation

The selective CO<sub>2</sub> hydrogenation to FA was evaluated in a batch Fischer-porter reactor using Ru clusters/SILP-BF<sub>4</sub> catalyst in an aqueous solution of 3-n-butyl-1-methylimidazolium acetate (BMIm.OAc) IL at 87 °C under a 32-bar CO<sub>2</sub>/H<sub>2</sub> gas mixture (Table 2). No FA was observed when the reaction was performed solely in water. Interestingly, 0.12 M of FA was generated with 96 TONs when an aqueous solution of BMIm.OAc IL was used (Table 2, entry 1). This efficient activity in aqueous solution of BMIm.OAc IL is attributed to the highly efficiently of the BMIm.OAc IL that absorbs and reacts reversibly with CO<sub>2</sub> to yield bicarbonate (HCO<sub>3</sub><sup>-</sup>) [14]. Moreover, this IL solution can act as IL-water proton buffer solution to stabilise the generated “free” FA during CO<sub>2</sub> hydrogenation. By the introduction of Me-THF and 1,4-dioxane solvents in BMIm.OAc/H<sub>2</sub>O, the activity was reached to 120 and 132 TON, respectively (Table 2, entries 3–4). On note, almost three-fold (0.50 M) FA was achieved when DMSO was used in combination with BMIm.OAc/H<sub>2</sub>O (Table 2, entry 5). This dominance of DMSO over other solvents may be because of the intermolecular interactions between IL and DMSO, which lead to loosest packing due to the hydrogen bonding of

**Table 2**Effect of different solvent on CO<sub>2</sub> hydrogenation to formic acid (FA) by Ru clusters/SILP-BF<sub>4</sub> catalyst.<sup>a</sup>

Entry	Media	FA [M]	TON
1	H <sub>2</sub> O	–	–
2	H <sub>2</sub> O/BMIm.OAc	0.12	96
3	Me-THF/BMIm.OAc/H <sub>2</sub> O	0.15	120
4	Dioxane/BMIm.OAc/H <sub>2</sub> O	0.17	132
5	DMSO/BMIm.OAc/H <sub>2</sub> O	0.50	396
6	DMSO/BMIm.OAc	0.12	96

[a] Reaction conditions: 20 mg Ru/SILP-BF<sub>4</sub> (3 % Ru wt.), 300 mg IL (1.51 mmol), 33 mg H<sub>2</sub>O (1.8 mmol), 2.84 g solvent (36.4 mmol), CO<sub>2</sub>/H<sub>2</sub> (1:2, 32 bar), 87 °C and 19 h. [b] TON/TOF were calculated on the basis of presence of active atoms of Ru [40].

imidazolium hydrogen atoms with DMSO and shifts the equilibrium to FA [59]. A small amount of H<sub>2</sub>O was necessary to accelerate the formation of bicarbonate (HCO<sub>3</sub><sup>-</sup>) and stabilize the formed FA through H-bonding [60].

Since a layer of the imidazolium-based ILs generates ionic-cages around the solid SiO<sub>2</sub> by the combination of their H-bonding and counter-ion pairs. It enriches the local density, tunes the IL orientation close to the surface to facilitate the substantial charge transfer and leading to the reconstruction of the interfacial ionic structure.[61,62] Hence these IL-cages/containers are akin to the membrane in which the geometric and electronic properties of the NPs can be modulated by the proper choice of the IL cations and anions that significantly impacted the diffusion of the reactants, intermediates, and products.[25,28] Of note, the hydrophilic and hydrophobic nature of the SILPs strongly tuned the catalytic activity of the Ru clusters/NPs during the hydrogenation of CO<sub>2</sub> to FA (Table 3, Fig. 5).

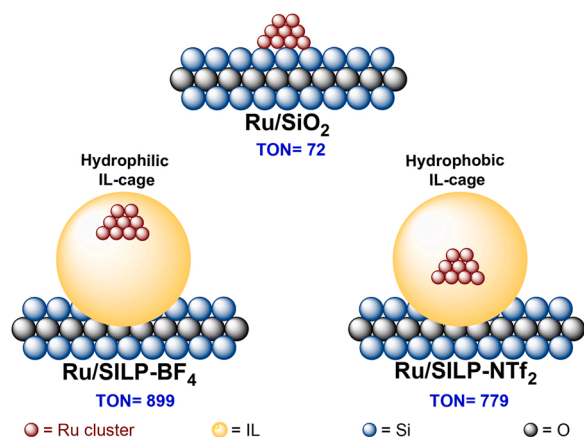
The hydrophilic SILPs (SILP-BF<sub>4</sub>) having hydrophilic anions (BF<sub>4</sub><sup>-</sup>) represented remarkable activity (889 TON, 1.13 M FA) as compared to the SILP containing hydrophobic NTf<sub>2</sub> anion (SILP-NTf<sub>2</sub>), which showed 779 TON and 0.98 M FA generation (Table 3, entries 1–2, Fig. 5). This influence can be attributed to hydrophilicity of the BF<sub>4</sub> anion in SILP, which caused the high concentration of the Ru clusters preferentially remained on the surface of the IL (as confirmed by the XPS analysis, Table 1). The hydrophilic nature of the support with confine spaces is akin to the catalytic membrane-like device, offering maximum catalytic active sites to activate CO<sub>2</sub> and H<sub>2</sub>. The opposite phenomenon was observed in hydrophobic SILPs-NTf<sub>2</sub> in which Ru NPs were penetrated deep into the support, as revealed by the XPS analysis (Table 1). This limited the access of CO<sub>2</sub> and H<sub>2</sub>, resulting low catalytic activity (Fig. 5). It is noteworthy that this IL effect on the catalytic activity was confirmed when pristine Ru/SiO<sub>2</sub> was used in which no IL was presented. The catalytic activity was greatly dropped to 72 TON, resulting in only 0.09 M FA formation (Table 3, entry 3). The presence of BF<sub>4</sub> anion induces the hydrophilicity in SILP-BF<sub>4</sub> that keeps the NPs on the surface, while the NTf<sub>2</sub> anion generated the hydrophobicity in SILP-NTf<sub>2</sub> to keep the NPs close to the surface.[41].

CO<sub>2</sub> hydrogenation was also investigated at different temperature from 60° to 120°C by Ru clusters/SILP-BF<sub>4</sub> catalyst (Fig. 6a). Interestingly, no FA generation was detected below 65 °C. At 65 °C, a small amount of FA was attained. The FA generation significantly increased with the increased of temperature. When the temperature was reached to 87 °C, about 0.5 M FA was obtained with 396 TONs. While the 0.82 M and 1.2 M FA was achieved at 105 °C and 120 °C, respectively. Of note that no degradation of the BMIm.OAc IL and DMSO was found under our standard conditions at 120 °C, as confirmed by <sup>1</sup>H and <sup>13</sup>C NMR analyses of the crude reaction (Fig. S6). No CO was detected at this temperature (120 °C). An Arrhenius plot was attained on the linear fitting of ln TOF versus temperature from 65° to 120°C and resulted an apparent activation energy of 52 ± 3 kJ/mol (Fig. 6b). Note that Ea is slightly lower than the activation energies reported for the FA obtained by using Ru-based complexes (58–93 kJ/mol) under similar reaction media. [16, 32] Furthermore, the rate of FA generation was also monitored at

**Table 3**CO<sub>2</sub> hydrogenation to HCO<sub>2</sub>H by different catalysts at 87 °C.<sup>a</sup>

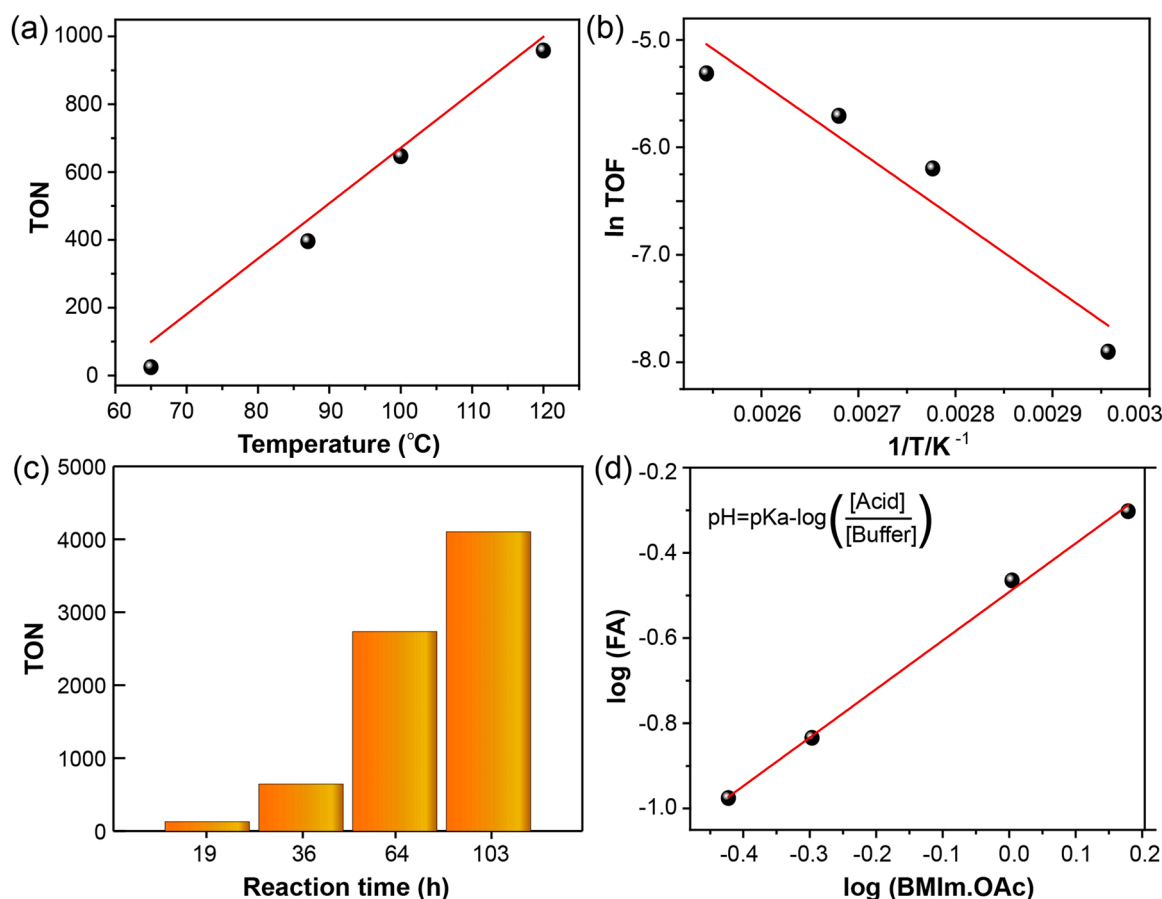
Entry	Cat.	FA [M]	TON
1	Ru/SILP-BF <sub>4</sub>	1.13	899
2	Ru/SILP-NTf <sub>2</sub>	0.98	779
3	Ru/SiO <sub>2</sub>	0.09	72
4 <sup>b</sup>	Ru/SILP-BF <sub>4</sub>	1.27	4103

[a] Reaction conditions: 20 mg Ru/SILP-BF<sub>4</sub> (3 % Ru wt.), 300 mg IL (1.51 mmol), 33 mg H<sub>2</sub>O (1.8 mmol), 2.84 g solvent (36.4 mmol), CO<sub>2</sub>/H<sub>2</sub> (1:2, 32 bar) and 64 h. [b] 5.0 mg Ru/SILP-BF<sub>4</sub> (3 % Ru wt.), 400 mg IL (2.02 mmol), 33 mg H<sub>2</sub>O (1.8 mmol), 2.84 g DMSO (36.4 mmol), CO<sub>2</sub>/H<sub>2</sub> (1:2, 32 bar) and 64 h.



**Fig. 5.** Graphical representation of the IL-cage effect of hydrophilic (BF<sub>4</sub>) and hydrophobic (NTf<sub>2</sub>) anions in SILPs having Ru clusters/NPs on the CO<sub>2</sub> hydrogenation to FA.

different reaction time, which augmented linearly with the time (Fig. 6c). At 19 h, 129 TON was obtained that reached to 645 at 36 h with the formation of 0.2 m FA. A significant amount of FA of 0.85 and 1.27 was achieved at 64 and 103 h with 2735 and 4103 TONs, respectively. A total of 2.18 M FA was reached with 7032 TONs. Our catalytic system demonstrated a higher amount of free FA formation and TONs as compared to previously reported heterogeneous catalysts (Table S2, Supporting information).



**Fig. 6.** Effect of temperature of CO<sub>2</sub> hydrogenation to FA (a) and Arrhenius plot (b). Reaction conditions: 20 mg Ru/SILP-BF<sub>4</sub>, 300 mg IL (1.51 mmol), 33 mg H<sub>2</sub>O (1.8 mmol), 2.84 g solvent (36.4 mmol), CO<sub>2</sub>/H<sub>2</sub> (1:2, 32 bar) and 18 h. (c) Time effect vs TON. Reaction conditions: 5 mg Ru/SILP-BF<sub>4</sub>, 400 mg IL (2.02 mmol), 33 mg H<sub>2</sub>O (1.8 mmol), 2.84 g solvent (36.4 mmol), CO<sub>2</sub>/H<sub>2</sub> (1:2, 32 bar) and 87 °C. (d) Relationship between FA and BMIm.OAc IL. Reaction conditions: 20 mg Ru/SILP-BF<sub>4</sub>, 2.84 g solvent (36.4 mmol), 33 mg H<sub>2</sub>O (1.8 mmol), CO<sub>2</sub>/H<sub>2</sub> (1:2, 32 bar), 18 h and 87 °C.

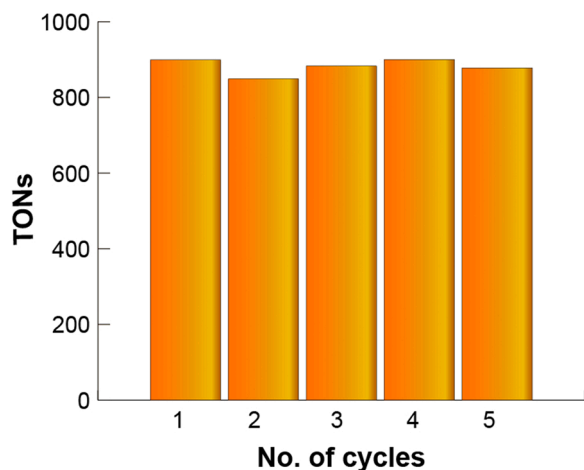
Moreover, the buffer capacity of the BMIm.OAc IL in our catalytic system was confirmed by obtaining a linear relationship between the FA formed and the amount of the IL (Fig. 6d). The amount of FA increased with the increased of IL amount that provided evidence that IL acted as a buffer. This behavior is consisted by Henderson-Hasselbach equation for buffering systems. [63,64] The IL plays a multiply role; activates the CO<sub>2</sub>, stabilize the active intermediates and formed FA as well as stabilize the NPs.

A labelling experiment using <sup>13</sup>CO<sub>2</sub> was performed to determine the source of carbon in FA generation. <sup>13</sup>C NMR clearly showed a strong signal at about 166 ppm that was attributed to the H<sup>13</sup>CO<sub>2</sub>H (Fig. S8). Whereas, HNMR spectrum of the same solution also represented the formation of H<sup>13</sup>CO<sub>2</sub>H from <sup>13</sup>CO<sub>2</sub> (Fig. S8). Furthermore, Ru clusters/SILP-BF<sub>4</sub> catalyst was recycled five times and showed its stability to the generation of FA (Fig. 7).

### 3.3. Catalytic CO<sub>2</sub> hydrogenation mechanism

Hydrogenation of CO<sub>2</sub> to FA involved two pathways. One is the direct hydrogenation of CO<sub>2</sub> to FA while the second pathway involves the hydrogenation of CO<sub>2</sub> to formate salts. Until now it has been widely accepted that the mechanism involves the formation of the carbonates which undergo hydrogenation by the metal-hydrides species to generate formate species. While in aqueous solution, HCO<sub>3</sub><sup>-</sup> are also generated along with the carbonates under basic and/or buffer environment. The hydrogenation of HCO<sub>3</sub><sup>-</sup> has been ignored. An aqueous solution of the BMIm.OAc IL efficiently absorbs and reacts reversibly with CO<sub>2</sub> yielding HCO<sub>3</sub><sup>-</sup> [14,65–67]. We propose that the generation of the FA originates





**Fig. 7.** Reaction conditions: 20 mg Ru/SILP-BF<sub>4</sub>, 300 mg IL (1.51 mmol), 33 mg H<sub>2</sub>O (1.8 mmol), 2.84 g solvent (36.4 mmol), CO<sub>2</sub>/H<sub>2</sub>(1:2, 32 bar) and 64 h.

from the hydrogenation of the HCO<sub>3</sub><sup>-</sup> rather than the direct hydrogenation of the CO<sub>2</sub> in an aqueous solution. For this purpose, DFT calculation was performed to investigate the hydrogenation of HCO<sub>3</sub><sup>-</sup> to FA on metallic Ru (0001) surface.

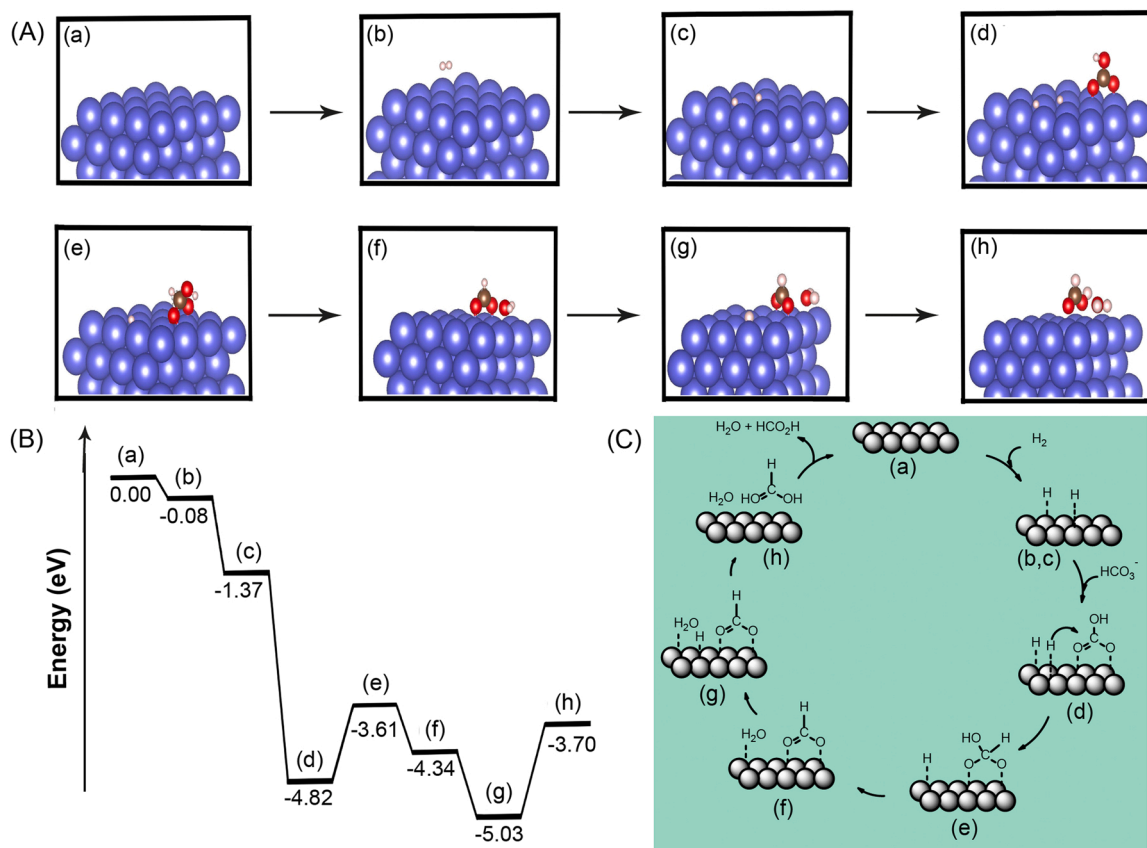
To understand the structure-dependent activity of the Ru in the hydrogenation of HCO<sub>3</sub><sup>-</sup> at atomic level, Density Functional Theory (DFT) calculations were conducted. These calculations were simulated at 298.15 K. A surface geometry of P63/m of Ru 0001 surface was built (Fig. 8A). It has been widely accepted that H<sub>2</sub> undergoes hemolytic

dissociation over the Ru surface and the rate determination of the reaction was the subsequent hydrogenation (Fig. 8A, step c). This is followed by the adsorption of the HCO<sub>3</sub><sup>-</sup> generated by the BMIm.OAc IL that undergoes hydrogenation to produce formate (HCO<sub>2</sub><sup>-</sup>) as shown in Fig. 8A (Step d). The hydrogenation of the formed HCO<sub>2</sub><sup>-</sup> occurred toward FA.

The calculated energy profile for the hydrogenation of HCO<sub>3</sub><sup>-</sup> involves eight steps (Fig. 8B). The starting step is the metallic Ru 0001 surface (a). In the following step (b), the H<sub>2</sub> molecule is adsorbed on the surface with adsorption energy of -0.08 eV. The dissociation of the H<sub>2</sub> occurs on Ru with a barrier of -1.37 eV (step-c). Following this, HCO<sub>3</sub><sup>-</sup> is adsorbed, which undergoes reduction by the attack of hydride with a barrier of -3.61 eV (step-e). This intermediate subsequently generates formate (HCO<sub>2</sub><sup>-</sup>) along with H<sub>2</sub>O with the energy barrier of -4.34 eV as shown in step-f. The insertion of H<sup>+</sup> to the oxygen of HCO<sub>2</sub><sup>-</sup> generated FA with an energy reaction of over -3.70 eV.

#### 4. Conclusions

SILPs were decorated with naked Ru clusters and NPs by the magnetron sputtering. The presence of IL anions (BF<sub>4</sub><sup>-</sup> and NTf<sub>2</sub><sup>-</sup>) in SILPs kinetically controlled the growth of incoming sputter Ru atoms into clusters and/or nanoparticles. SILPs containing hydrophilic anion (BF<sub>4</sub><sup>-</sup>) facilitated the formation of Ru clusters, while SILPs with hydrophobic anion (NTf<sub>2</sub><sup>-</sup>) resulted in the formation of highly dispersed ultra-small (1.8 ± 0.3 nm) NPs. Moreover, the IL in SILPs generated the confined spaces akin to the solvent-cages that effectively controlled the selective CO<sub>2</sub> hydrogenation to base-free FA. The presence of the hydrophilic anion (BF<sub>4</sub><sup>-</sup>) in SILP promoted a higher population of the Ru clusters on the support surface, providing maximum catalytic active sites for the



**Fig. 8.** (A) Ball-and-stick illustrations of the atomic structures: (a) Top and side views of the clean Ru surface, (b) H<sub>2</sub> near (0001) surface, (c) displaying binding of H<sub>2</sub> on (0001) surface, (d) cleavage of H<sub>2</sub> to H<sup>\*</sup> atoms, (e) adsorption of HCO<sub>3</sub><sup>\*</sup>, (f) H<sup>\*</sup> insertion to carbon of HCO<sub>3</sub><sup>\*</sup> (g) the formation of HCO<sub>2</sub><sup>\*</sup> and H<sub>2</sub>O<sup>\*</sup> and (h) H<sup>\*</sup> insertion to O of HCO<sub>2</sub><sup>\*</sup> to form HCO<sub>2</sub>H. (B) DFT-calculated adsorption energy, in eV. (C) A reaction pathway for the hydrogenation of HCO<sub>3</sub><sup>-</sup> to FA on Ru (0001).

activation of the CO<sub>2</sub> and H<sub>2</sub> to FA that led to a significant enhancement in FA generation. The opposite phenomenon was observed in SILPs with hydrophobic NTf<sub>2</sub> anion in which Ru NPs were migrated deep into the support, thereby providing relatively limited access to CO<sub>2</sub> and H<sub>2</sub>. As prepared Ru clusters/SILP catalyst showed the remarkable generation of the FA with a yield of 2.2 M and 7305 TONs in BMIm.OAc/DMSO/H<sub>2</sub>O media at 87 °C. The mechanism was confirmed by DFT calculations that followed the reaction pathway of the hydrogenation of HCO<sub>3</sub>\* to the FA.

## Associated content

None.

## Supporting Information

Experimental details about the <sup>13</sup>C and <sup>29</sup>Si CP-MAS analyses and TGA analyses of the SILPs. HAADF-STEM and XPS analyses of Ru/SILPs and Ru/SiO<sub>2</sub>.

## CRediT authorship contribution statement

All the authors contributed equally.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data Availability

Data will be made available on request.

## Acknowledgment

We are grateful to CAPES (001), FAPERGS (22/2551-0000386-9 and 18/2551-0000561-4) and CNPq (406260/2018-4) for financial support. J.D. is a fellow of the “Maria Zambrano program” at the University of Murcia (Spain). R.B.P. acknowledges CNPq (grant 309599/2021-0) for financial support as well as LaMCAD-UFG, CENAPAD-SP and Cluster Euler/CeMEAI for providing the computational resources. MVC thanks to CAPES (22/2551-0000544-6). DE is grateful to Bluenano for providing Sputtering facility.

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123315](https://doi.org/10.1016/j.apcatb.2023.123315).

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